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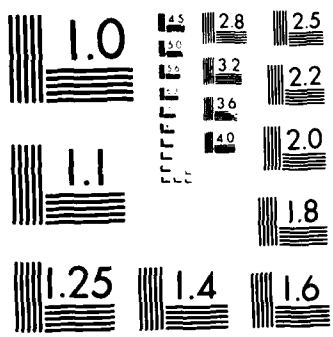

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Laser-Stimulated Vibrational Excitation of an Adspecies Studied by a Generalized Master Equation: Neutral Atomic Hydrogen on Hydrated KCl(001)

by

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Abstract

Vibrational energy transfer between an IR laser, a solid surface and an adatom is studied by a generalized master equation which includes memory effects. Numerical problems associated with the temporally delocalized memory kernel are overcome by introducing the isomnesic approximation. Results obtained for time scales ranging from 2 ps to 2 μs for $H(H_2O)/KCl(001)$ show that effective vibrational excitation is possible with low power lasers ($1\ W/cm^2$) in spite of fast phonon relaxation. Detailed time-evolution of the system is seen to differ radically from that predicted by Markovian theories, even for fairly long time scales.

I. Introduction

Developments in the experimental study of clean, well-characterized solid surfaces and surface processes such as scattering, adsorption, desorption and migration in the presence of laser radiation have resulted in important technological applications (e.g., laser-assisted vapor deposition of microcircuits). The underlying dynamics of these heterogeneous systems is a many-body problem involving the elementary excitations of the solid and its surface, such as phonons, electrons and plasmons, the degrees of freedom of the adsorbed species or gas molecules, and those of the laser.[1,2] The excitation process can be considered as direct laser-pumping of the substrate leading to a primarily non-selective thermal effect, or a pumping of the adsorbed species, which can be selective in the sense that only a single degree of freedom is excited by the laser. The resulting energy absorption and the dissipation involving all other degrees of freedom govern the overall chemical process.[3-8]

In this work, the vibrational excitation of a prototype system, viz. the adsorptive bond (adbond) between an atom and a surface is studied. This system is not in the same category as those in which internal vibrational modes of an adsorbed molecule are excited, with subsequent energy transfer to the adbond.[7,9] It is substantially simpler, in view of the aim of this work, which is to investigate the mechanisms involved in IR laser-stimulated surface processes (LSSP) using a treatment which is as close to first-principles as possible. One of the fundamental questions addressed is whether a low-power laser, because of its coherence, can deposit large amounts of energy into a specific mode of a system (such as an adbond) which is coupled to energy sinks, such as phonons, which are not infinite.

Early classical treatments[10] of the problem and phenomenological quantum treatments[4,5] provided conflicting answers to this question. Recent, more fundamental studies[8] have suggested that extremely high laser powers would be needed to effectively desorb an adspecies. However, our preliminary work[11] showed that a very small degree of detuning between the laser and energy levels of the system excluded the possibility of long-term energy absorption. The reason for this behaviour is seen to be the oscillatory nature of the laser energy absorption "rate" (actually, the memory kernel) for the adbond, with a frequency related to the detuning, typically a small percentage of the laser frequency itself, viz. ~ 10^{10}-10^{11} s^{-1}. Thus, for processes lasting over a few hundred picoseconds, substantial cancellations in the overall absorption can be expected, and only a very high-power laser would be able to compete with the loss of energy from the adbond to phonons through relaxation effects. In view of this, the systems chosen here have little or no detuning, viz. systems with one bound-to-bound transition exactly resonant with the laser frequency and another very close to or equal to the Debye frequency of the solid. This represents an ideal situation which emphasizes the coherent nature of laser radiation.

The widely varying temporal behaviour of dynamical systems far from equilibrium is well established. From a fundamental point of view, theoretical treatments of such systems depend crucially on the time scales being considered. The most common long-time limit, for example, allows a description of energy transfer in terms of average relaxation rates in the Markovian approximation, where approach to equilibrium is assumed to be monotonic. Non-Markovian behaviour is assumed to last for extremely short times compared to typical relaxation times of the system. The forces are considered to be random, with a very short correlation time. Resonant excitation with a low-power laser does not satisfy these conditions, and

one should expect non-Markovian behaviour to persist for times that increase with decrease in laser power. Whether the two approaches lead to the same steady state is also open to question.

Non-Markovian effects are conveniently treated by using a generalized master equation (GME) to describe the time-evolution of the adbond (the "relevant" system) with the laser and phonon fields as two uncoupled irrelevant systems (reservoirs).[12-14] The Liouville equation for such a system is conveniently solved by using the Zwanzig projection-operator technique[12] and results in a set of coupled integrodifferential equations for the occupation probabilities P_S of states $|S\rangle$ of the adbond:[14]

$$\dot{P}_S(t) = \sum_{S' \neq S} \int_0^t dt' \, [K_{SS'}(t-t')P_{S'}(t') - K_{S'S}(t-t')P_S(t')] \, , \qquad (1)$$

where the memory kernels $K_{SS'}$ include contributions due to the phonon field $K^{(p)}$ and the radiation field $K^{(r)}$:

$$K_{SS'}(t) = K_{SS'}^{(p)}(t) + K_{SS'}^{(r)}(t). \qquad (2)$$

Using a one-dimensional lattice and a Debye model to describe the lattice vibrations, we have obtained $K_{SS'}^{(p)}$ in a closed form which involves a summation over all lattice positions ℓ and number of phonons n independently.[11,15] The former is due to a summation of pair potentials between the adatom and the lattice atoms, while the latter results from an expansion of $\exp[y_{\ell\ell'}(t)]$ in a Taylor series, where $y_{\ell\ell'}(t)$ is the lattice displacement correlation function

$$y_{\ell\ell'}(t) = \langle\langle u_\ell(t) u_{\ell'} \rangle\rangle \, . \qquad (3)$$

Using techniques described elsewhere,[11] $y_{\ell\ell'}(t)$ can be obtained in closed form as

$$y_{\ell\ell'}(t) = R_{\ell\ell'}(t) + i \, I_{\ell\ell'}(t) \, , \qquad (4)$$

where $R_{\ell\ell'}$ and $I_{\ell\ell'}$ involve products of polynomials in t and cos $(\omega_D t)$ or sin $(\omega_D t)$, and ω_D is the Debye frequency. The phonon part of the memory kernel can then be written in terms of all the system parameters as follows:

$$K_{SS'}^{(p)}(t) = A_p \sum_n (B_p)^n \sum_{\ell\ell'} \sum_{\mu\mu'} (\mu\mu')^n \times \lambda_{\ell\ell'\mu\mu'}(S\leftarrow S')[\tilde{E}_{n\ell\ell'}(t)\cos(\omega_{SS'}t) + \tilde{O}_{n\ell\ell'}(t)\sin(\omega_{SS'}t)]. \tag{5}$$

Here

$$A_p = 8\left(\frac{D_e^{(0)}}{\hbar}\right)^2 , \tag{6}$$

$$B_p = 6\,(\beta^{(0)}k_bT)^2/m_S\hbar\omega_D^3 , \tag{7}$$

$$\tilde{E}_{n\ell\ell'}(t) = \sum_{j_e=0,2,4\ldots} \frac{(-1)^{j_e/2}}{j_e!(n-j_e)!} R_{\ell\ell'}^{n-j_e}(t)\, I_{\ell\ell'}^{j_e}(t) , \tag{8}$$

$$\tilde{O}_{n\ell\ell'}(t) = \sum_{j_o=1,3,5..} \frac{(-1)^{(j_o-1)/2}}{j_o!(n-j_o)!} R_{\ell\ell'}^{n-j_o}(t)\, I_{\ell\ell'}^{j_o}(t) , \tag{9}$$

$$\max(j_e, j_o) \leq n . \tag{10}$$

B_p is a smallness parameter which dictates, in part, the convergence properties of the expansion in number of phonons n. It is of the order of .02 for common temperatures T and common Debye frequencies (k_B is the Boltzmann constant and m_s the mass of a lattice atom). μ and μ' take on the values 1 and 2. The supermatrix λ involves powers of exp(a) and exp($\ll u^2 \gg$) and the matrix elements

$$E_{SS'}^{(\mu)} = \langle S|e^{\mu(z-z_0^{(0)})}|S'\rangle \tag{11}$$

where a is the lattice constant, u is the lattice displacement operator, and z is the distance of the adatom from the equilibrium position of the outermost lattice atom. The frequencies $\omega_{SS'}$ correspond to transitions between levels $|S\rangle$ and $|S'\rangle$ of the adbond represented by a Morse potential with depth $D_e^{(0)}$, equilibrium distance $z_0^{(0)}$ and exponent $\beta^{(0)}$.

The radiation part $K_{SS'}^{(r)}$ of the memory kernel is given by

$$K_{SS'}^{(r)}(t) = A_r z_{S'S} z_{SS'} \cos(\omega_L - |\omega_{SS'}|)t, \tag{12}$$

where $z_{SS'} = \langle S|z|S'\rangle$. The amplitude $A_r = (Ie_0^2/\varepsilon_0 ch^2)$ is proportional to the laser frequency I and the square of the charge separation e_0 between the adspecies and the surface.

The complicated form of $R_{\ell\ell'}$ and $I_{\ell\ell'}$ precludes analytic solution of the GME. Numerical solution is made difficult by the presence of high frequencies in $K_{SS'}^{(p)}$ and the large difference in the magnitudes of A_r($\sim 10^{17}$ s^{-2} for a 1 W/cm^2 laser) and A_p($\sim 10^{29}$ s^{-2} for $D_e^{(0)}$ = 0.1 eV). One can only solve the exact GME for a few periods of oscillation of $K_{SS'}$, which amounts to a few picoseconds.

Examination of a typical phonon kernel, Fig. 1, shows that it has substantial amplitude only for times of the order of a Debye period τ_D, representative of phonon correlation times. The laser kernel, on the other hand, has constant amplitude for the case $\omega_L = \omega_{SS'}$ for a given pair of levels (S,S'). For times larger than τ_D, the integrated effect due to $K_{SS'}^{(p)}$ will be unchanging because of cancellations, whereas that due to $K_{SS'}^{(r)}$ will be cumulative. We have recently demonstrated this effect[11] using the exact GME (with a very high laser power in order for the effect to manifest itself in the very short time for which solution was possible), and predicted, via extrapolation arguments, that effective pumping of the

adbond with a low-power laser would be possible if the long-time regime could be examined. We present here an actual calculation of this long-time behaviour using low-power lasers, and find that the average adbond energy, given by

$$E(t) = \sum_S E_S P_S(t) \tag{13}$$

where E_S are eigenvalues of the zeroth order adbond Hamiltonian, rises rapidly after an initial loss to the phonon field, and exhibits a decidedly non-Markovian pattern throughout.

The approximations required for the long-time treatment are described in Section II. The resulting probability and energy profiles are presented in Section III, where comparison is made with the exact results (for a short-time scale) and with a Markovian limit.

II. The Isomnesic (Constant-Memory) Approximation

We begin with the assertion that the physically important situation is one where the laser frequency and the Debye frequency equal different transition frequencies $\omega_{SS'}$ of the adbond.[11] For this case $K^{(r)}_{SS'}(t)$ becomes a constant $k_{SS'}$ (from the term with $|\omega_{SS'}| = \omega_L$) plus oscillating terms which we ignore in the sense of the rotating-wave approximation.[16] The phonon term, $K^{(p)}_{SS'}(t)$, has a complicated behaviour typified by $K^{(p)}_{03}(t)$ in Fig. 1, but we note that it has appreciable magnitude for times $\lesssim 2$ ps, and almost vanishes subsequently. If the mesh size of our theoretical experiment is no less than 2 ps, we can treat $K^{(p)}_{SS'}(t)$ as a delta function, so that, from Eq. (2),

$$K_{SS'}(t) = \Omega_{SS'}\,\delta(t) + k_{SS'} \quad . \tag{14}$$

where

$$\Omega_{SS'} = \int_0^\infty dt\, K^{(p)}_{SS'}(t) \quad . \tag{15}$$

In Eq. (14), the first term, originating from the coupling of the adbond to the phonons, is the amnesic or Markovian term, and would lead, in the absence of the laser term, to the elimination of all memory effects. The second term, due to the resonant laser coupling, is the isomnesic non-Markovian term, and represents a constant memory effect all the way back to t=0.

The subsequent treatment is simplified by defining "diagonal" elements Ω_{SS} as

$$\Omega_{SS} = - \sum_{S' \neq S} \Omega_{SS'} \tag{16}$$

and similarly for k_{SS} , and by introducing the vector notation $\underline{P}(t) \equiv \{P_S(t)\}$ and matrix notation $\underline{\underline{\Omega}} \equiv \{\Omega_{SS'}\}$, $\underline{\underline{k}} \equiv \{k_{SS'}\}$, etc. The exact GME may be written as

$$\dot{\underline{P}}(t) = \int_0^t dt' \, \underline{\underline{K}}(t-t') \cdot \underline{P}(t') \; ; \tag{17}$$

in the isomnesic approximation (IA) it becomes

$$\dot{\underline{P}}(t) = \underline{\underline{k}} \cdot \int_0^t dt' \, \underline{P}(t') + \underline{\underline{\Omega}} \cdot \underline{P}(t) \; . \tag{18}$$

Formally this can be solved without any further approximations. Differentiating both sides of Eq. (18) we get the second-order differential equation

$$\ddot{\underline{P}}(t) = \underline{\underline{k}} \cdot \underline{P}(t) + \underline{\underline{\Omega}} \cdot \underline{P}(t) \; , \tag{19}$$

whose Laplace transform,

$$\underline{\underline{M}}(s) . \, \underline{P}(s) = \underline{T}(s) \; , \tag{20}$$

where

$$\underline{\underline{M}}(s) \equiv \underline{\underline{k}} + s\underline{\underline{\Omega}} - s^2 \underline{\underline{\Delta}} \; , \tag{21}$$

$$\underline{T}(s) \equiv - s\underline{P}(0) \; . \tag{22}$$

and $\underline{P}(s)$ is the Laplace transform of $\underline{P}(t)$, is easily inverted using the Heaviside expansion theorem.

While this effectively eliminates the non-Markovian bottleneck, it is instructive to generate solutions of a Markovian version of this class of

problems. To do this, we have to make provisions for localizing $K_{SS'}^{(r)}$ in time. This brings to the fore the pervasive issue of time scales in dynamical many-body systems, our specific question being the relative degree of localization ascribable to $K_{SS'}^{(p)}$ and $K_{SS'}^{(r)}$. If the laser radiation is localized as a pulse, it can still extend over a period of time much longer than the extent of $K_{SS'}^{(p)}(t)$. In other words, the delta function representing $K_{SS'}^{(p)}(t)$ may be quite different from the delta function representing $K_{SS'}^{(r)}(t)$, and the former may in fact not really be considered as localized with respect to the latter. With these provisos in mind, we can proceed to write the Markovian version of Eqs. (14), (17), (19) and (20):

$$\underline{\underline{K}}(t) = (\underline{\underline{\Omega}} + \underline{\underline{f}})\, \delta(t) \,, \tag{23}$$

$$\dot{\underline{P}}(t) = \underline{\underline{W}} \cdot \underline{P}(t) \,, \tag{24}$$

$$\underline{\underline{J}}(s) \cdot \underline{P}(s) = \underline{U} \,, \tag{25}$$

where

$$\underline{\underline{f}} = \underline{\underline{k}}\, \tau \,, \tag{26}$$

$$\underline{\underline{W}} = \underline{\underline{\Omega}} + \underline{\underline{f}} \,, \tag{27}$$

$$\underline{\underline{J}}(s) = (\underline{\underline{\Omega}} + \underline{\underline{f}} - s\underline{\underline{\Delta}}) \,, \tag{28}$$

$$\underline{U} = - \underline{P}(0) \,, \tag{29}$$

and τ represents the actual extent of the laser signal or a variable time parameter. Equation (24) is the well-known Pauli master equation (PME).

III. Results of the Exact, Isomnesic and Markovian Approximations

The formalism of Sections I and II was applied to the system $H(H_2O)/KC\ell(001)$, the primary reasons for choosing which are the shallow adsorption potential well and the small number of bound states (7) it generates.[17] In Fig. 2 the results of the IA and the exact GME are compared for the system of references 11 and 15. The two are identical for $H(H_2O)/KC\ell$, and are not shown. While this is a short-time-scale comparison, the closeness

of the two leads us to expect the long-time IA results to be reliable. The Markovian approximation, on the other hand, cannot provide an unambiguous comparison because of large variations in the results for different values of τ , shown in Fig. 3. All subsequent figures, therefore present our IA results.

Figure 4 is a composite display of the function $E(t)$ obtained from results of Eq. (28) for six ranges of time differing by factors of 10 and for a laser intensity $I = 1\ W/cm^2$. It is seen that in going from a pico-second time range to a micro-second time range, the behaviour of the system changes dramatically. The early behaviour is dominated by fast energy transfer to phonon modes, completely overwhelming the slow laser pumping. The monotonic decay is representative of relaxation phenomena. For the 100 ps range, a false steady state seems to have been reached, but is in fact only an artifact of the large difference between A_r and A_p. The adbond energy starts to increase in the ns range, again suggesting a possible steady state. However, this is a transitional period during which the relative importance of the phonon terms and the laser terms starts to change. The latter, in fact, originate from a probability profile of the form $(Ae^{\alpha t} \cos \beta t - Be^{\alpha t} \sin \beta t)$, where $\alpha + i\beta$ are complex roots of

$$\det \underline{\underline{M}}(s) = 0 \ , \tag{30}$$

and $A + iB$ are complex coefficients obtained from $\underline{\underline{M}}(s)$ and $\underline{I}(s)$.

The phonon terms come from real roots and are therefore nonoscillatory. The magnitudes of the exponents α in the laser part of the solution are much smaller than corresponding exponents in the phonon term. This is responsible for the radically different nature of $E(t)$ in the different time regimes. Thus, the seemingly monotonic rise in $E(t)$ apparent in the 10 ns regime is seen to be only the early segment of a cycle which

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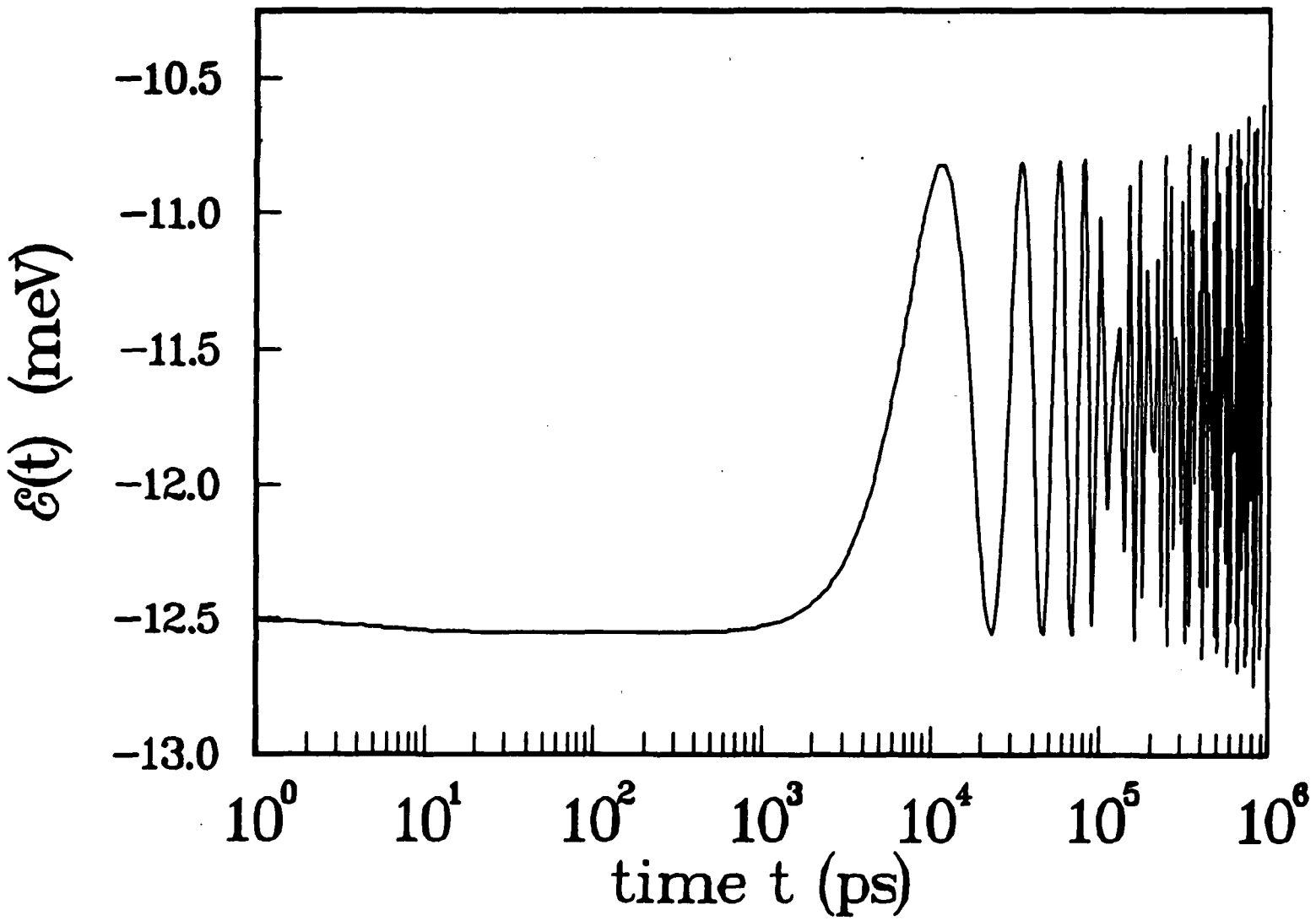
−10.5
−11.0
−11.5
−12.0
−12.5
−13.0
ℰ(t) (meV)
10^0
10^1
10^2
10^3
10^4
10^5
10^6
time t (ps)

Fig. 5

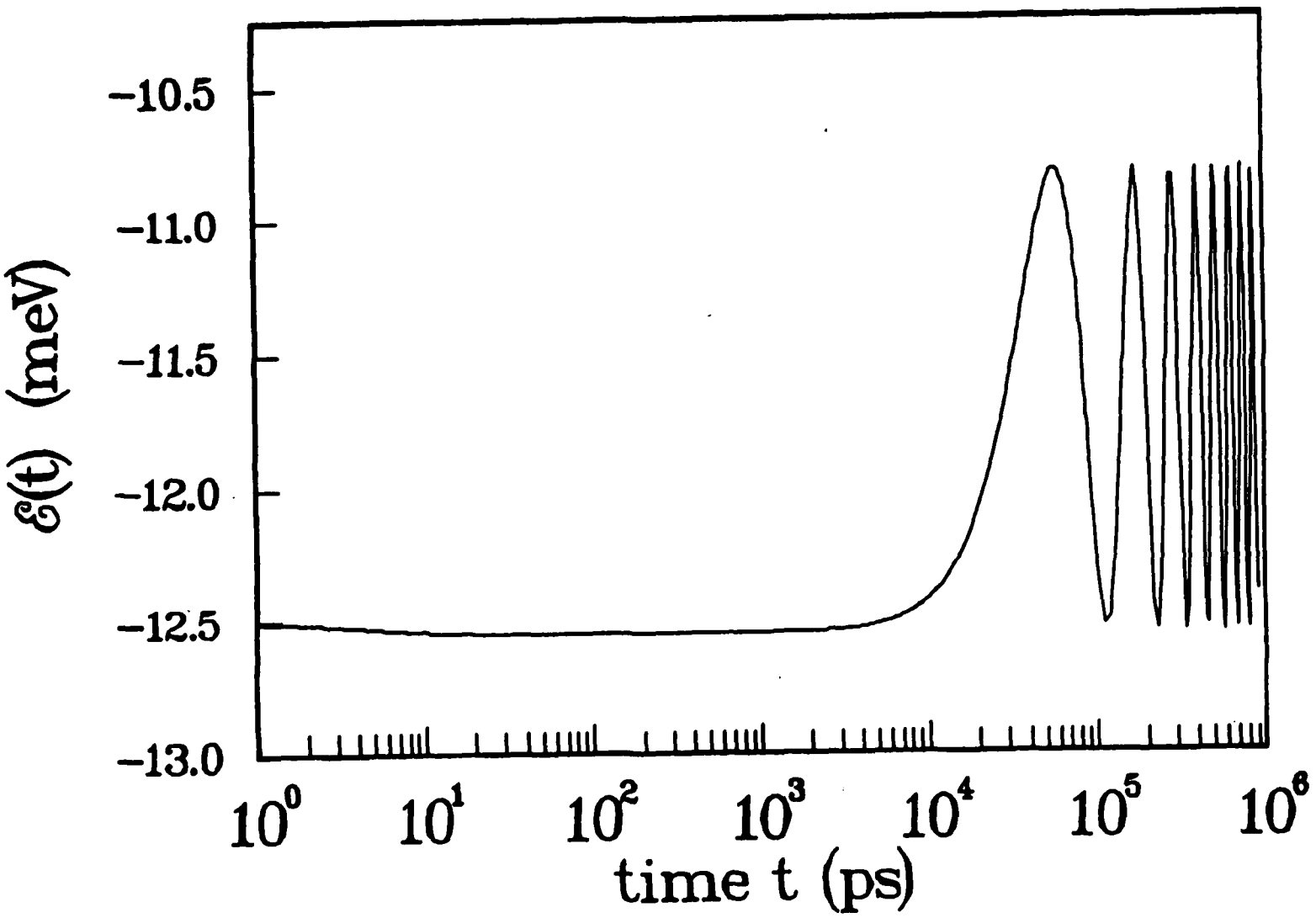
−10.5
−11.0
−11.5
−12.0
−12.5
−13.0
ε(t) (meV)
10^0
10^1
10^2
10^3
10^4
10^5
10^6
time t (ps)

Fig. 2

Beri/George Fig. 3

EXACT vs. *ISOMNESIC*

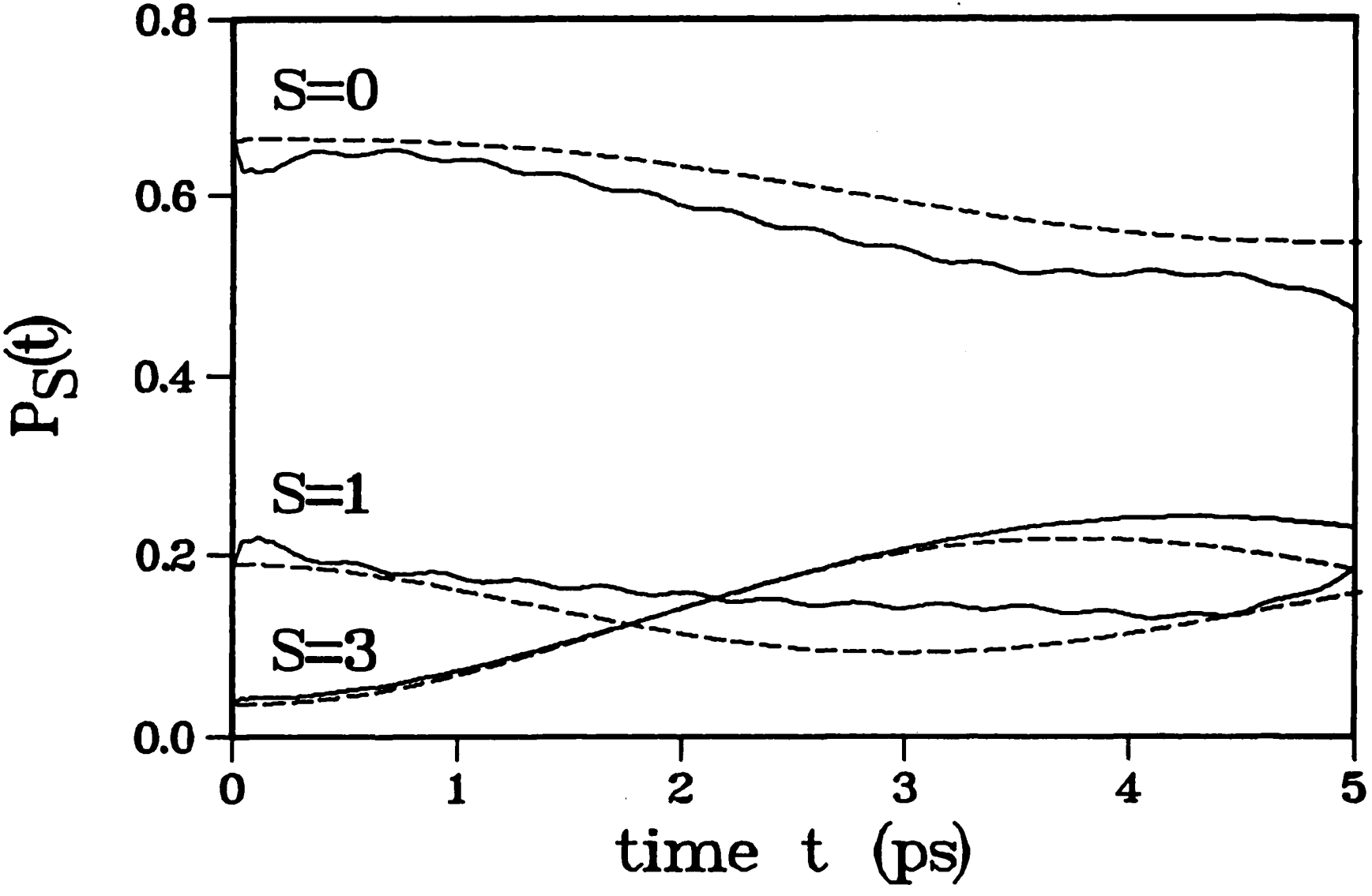

Fig. 2

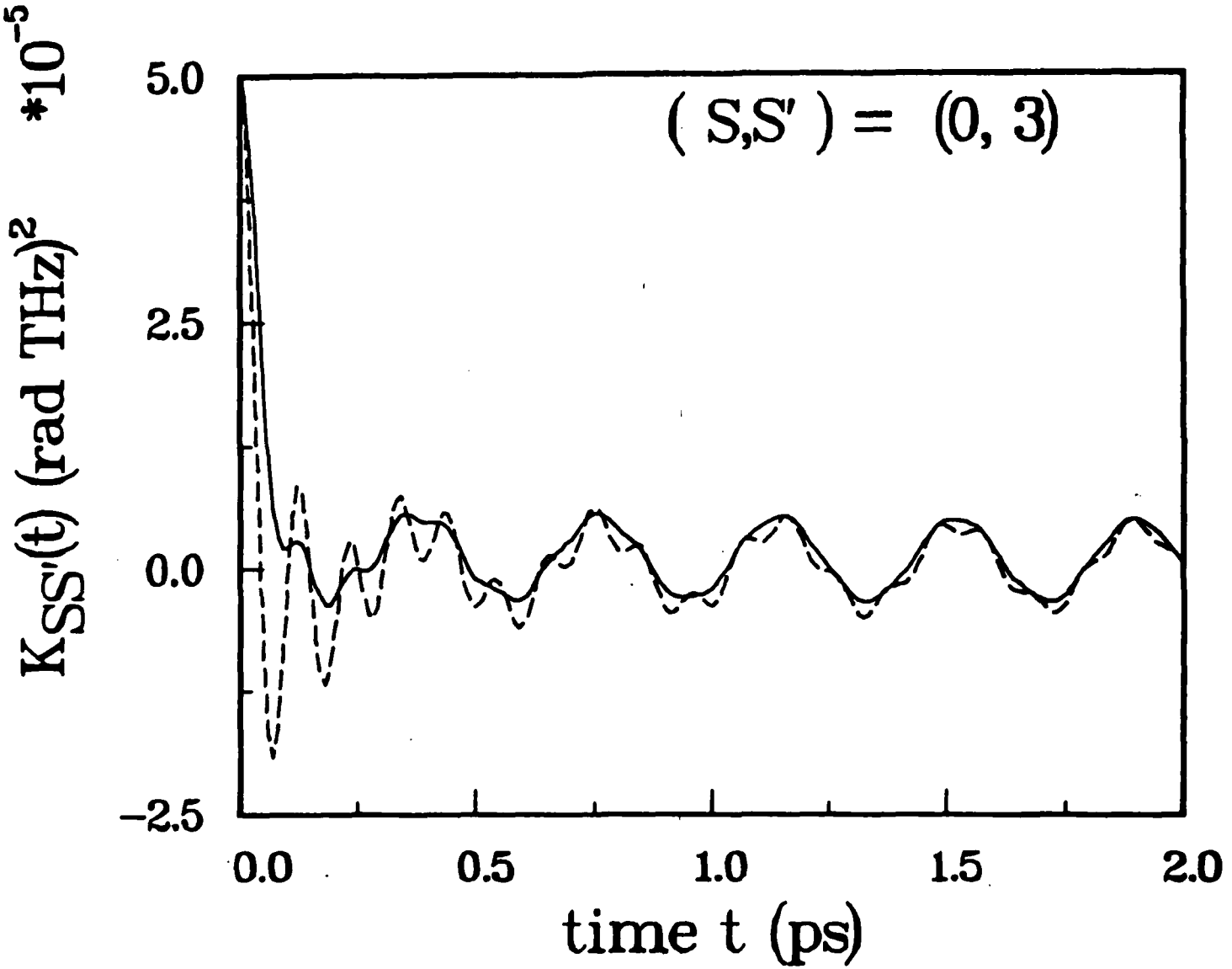
(S,S') = (0, 3)
$K_{SS'}(t)$ (rad THz)^2 *10^{-5}
5.0
2.5
0.0
−2.5
0.0
0.5
1.0
1.5
2.0
time t (ps)

Figure Captions

Fig. 1. Memory kernels $K_{SS'}^{(p)}(t)$ for (S,S') = (0,3). Solid line: 3→0; dotted line: 0→3.

Fig. 2. Probability profiles for system of references 11 and 15 obtained by solving the exact GME (solid line) and the isomnesic GME (dashed line).

Fig. 3. Average adbond energy E(t) obtained within the Markovian approximation for a range of values of the parameter τ.

Fig. 4. E(t) obtained by using the isomnesic approximation for time scales ranging from picoseconds to microseconds, for laser intensity I = 1 W/cm^2.

Fig. 5. Same as Fig. 4 for I = 25 W/cm^2.

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result, the sharp transitions assumed here will be broadened by a detuning-type effect, and estimates of the desorption rate presented above will have to be modified. However, the selectivity represented by the dominant T_1 energy-transfer process will be retained.

For a complete study of desorption, transitions to the continuum must be included, and at the outset it is difficult to predict which levels will be most important. Work in this direction is in progress, and represents a departure from the first-principles approach in the inclusion of the bound-to-continuum transitions. This, as well as a complete first-principles treatment of vibrational LSSP including desorption, will be presented in the near future.

Acknowledgments

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becomes evident in the 100 ns results and beyond. The frequency of this oscillation is seen to be $k_0^{\frac{1}{2}}$, where k_0 is the amplitude of the laser kernel $k_{SS'}$, and is essentially the Rabi frequency for the pair of levels resonant with the laser.

While the frequency of the long-term oscillations of P(t) and E(t) depends only on the laser term, being proportional to the square root of the intensity, the rate of onset of this behaviour depends on α which varies linearly as k_0 and inversely as the amplitude Ω_0 of the phonon kernel. Thus, increasing the laser power from 1 W/cm^2 to 25 W/cm^2 advances the onset time for the oscillatory state while increasing the frequency by a factor of 5, as displayed in Fig. 5.

Physically, the results of Figs. 4 and 5 can be interpreted in terms of desorption rates. Thus, the time required for $|A|e^{\alpha t}$ and $|B|e^{\alpha t}$ to become large enough so that the amplitude of E(t) in the oscillatory regime is substantially larger than the (t = 0) equilibrium Boltzmann value, is a reasonable measure of the desorption time to within an order of magnitude. This time is estimated by $\tau_D = \alpha^{-1}$. For our case,

$$\tau_D^{-1} = \alpha \simeq \cdot 5 \frac{k_0}{\Omega_0} \simeq (10^4 \text{ w}) \text{ s}^{-1} , \qquad (31)$$

where w is laser power in W/cm^2. Thus, for a 1 W/cm^2 laser, a hydrogen atom will stay adsorbed on the KCl(H_2O) surface for ~ 10^{-4} s on the average before desorbing, or at least becoming very highly excited. The data mentioned here is for T = 150 K.

It must be pointed out that a number of mechanisms whereby the desorption cross section could be modified are not included. Spontaneous decay, phase relaxation, phonon-phonon interaction and electron-hole pair creation are some of the ones being considered in extensions of this work. As a

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